3^{rd} Quarterly Status Report
Liquid-Phase Deposition of α-CIS Thin Layers
Contract # XDJ-3-30630-33

F. Ernst and P. Pirouz

Department of Materials Science and Engineering
Case Western Reserve University
10900 Euclid Avenue
Cleveland, Ohio 44106-7204

October 30, 2003

Since the last quarterly status report, submitted in August 2003, we have made further advances toward the deposition of single phase α-$CuInSe_2$ films. In the last report we identified problems with the wetting of the substrate as well as problems in the deposition of thin films due to the increased viscosity of the supercooled melt. The wetting problems were overcome as previously reported. However, as will be discussed below, the viscosity issue still remains an obstacle to successful deposition of thin films, as well as in successful preparation of thin foils for TEM (transmission electron microscopy) studies. Our last report described the initial construction of a liquid-phase deposition (LPD) reactor, utilizing the sliding boat technique to overcome these viscosity issues. Since then, considerable progress toward completion of this reactor has been made. We expect that the final completion of the reactor will be made before the submission of the next quarterly report.

Since August, we have also carried out thermogravimetric analysis (TGA) on various ingots to determine whether we need to consider the vapor pressure of selenium in the employment of the sliding boat LPD technique.

Specimen Preparation for TEM

Owing to the high viscosity of the Cu–In–Se melt, the thicknesses of the Cu–In –Se layers we have deposited so far has been relatively large: on the order of 10 to 15 μm. For high-quality absorber layers, the thickness needs to be reduced. Moreover, layer thicknesses of this order of magnitude cause problems with the preparation of specimens for TEM. The reason for this problem is that the adhesion of the layer to the substrate material decreases significantly with the thickness of the Cu–In–Se layer, increasing the likelihood for damaging the Cu–In–Se layer during the mechanical preparation required prior to the final thinning procedure.

In order to obtain some first TEM specimens anyway, we are continuing to deposit films via our initial method of tilting the melt over the substrate, but with layers of exceedingly large thickness, generated on *purpose*. An exceedingly large layer thickness facilitates the subsequent removal layer from the substrate, which significantly facilitates the preparation of TEM specimens compared to the case of a thick Cu-In–Se layer adherent to a substrate of a different material.

This solution is temporary and we expect that once the construction of the sliding boat reactor is completed, we shall be able to deposit thinner layers with better adhesion and substantially advance the quality of their microstructural characterization.

Thermogravimetric Analysis

Several methods currently used for the deposition of α-$CuInSe_2$ and $CuInS_2$ require post-deposition annealing treatments in Se- or S-rich atmospheres to yield the desired chalcopyrite phase with the 1:1:2 stoichiometry. However, even when the deposited material has the correct stoichiometry, a chalcogenide-rich atmosphere is usually employed to maintain this composition. For the final construction of the sliding boat LPD reactor we need to determine at what pressures we need to operate in order to maintain the composition of the starting ingot as well as the composition of the deposited film. Therefore TGA (thermogravimetric analysis) was employed to measure the mass loss of various ingots as a function of temperature.

Figure 1 shows the liquidus projection of the Cu-In-Se system. The shaded areas represent the primary phase fields of α-$CuInSe_2$. The symbols $I_n, n = 1 \ldots 4$ on the figure display the compositions for which we have prepared specimens.

Figure 2 is a TGA plot of all the ingots made with compositions designated in Figure 1 Figure 2 reveals that there is no significant weight loss due to vaporization of selenium from ingots with compositions in regions I_1 (a, b, and c) and I_2. Significant weight loss is observed only from the selenium-rich regions designated I_3 and I_4. Therefore, ingots with compositions in regions I_1 and I_2 should show no selenium loss during deposition and will not require the use of chalcogenide-rich atmospheres.

In conclusion, we have made further, substantial progress towards our goal of fabricating α-$CuInSe_2$ thin films by liquid-phase deposition. The status of the project is in agreement with the original plan of work.

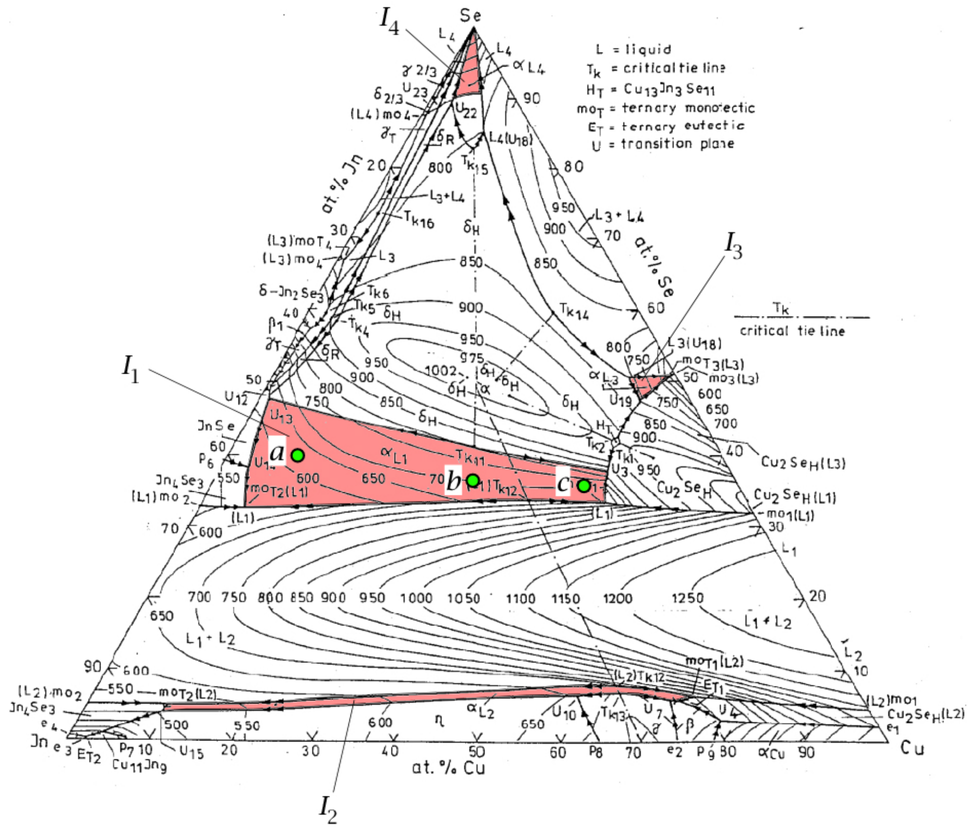

Figure 1: Liquidus projection of the Cu–In–Se system. The shaded areas represent the primary phase fields of α-$CuInSe_2$. The symbols $I_n, n = 1 \ldots 4$ on the figure display the compositions for which we have prepared specimens.

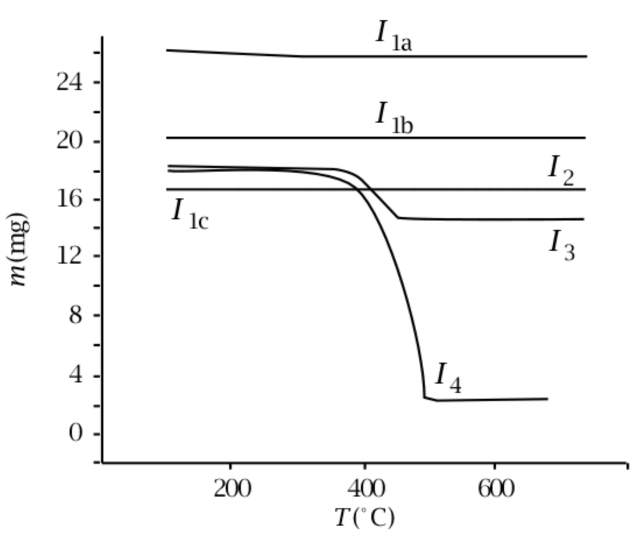

Figure 2: TGA plot of all the ingots made with compositions designated in Figure 1.